Microfluidic Distillation Utilizing Micro–Nano Combined Structure

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This paper reports a novel distillation method in microchannels. For the gas–liquid separator in the evaporator, hydrophilic–hydrophobic patterned microchannel structure was utilized. In order to control condensation of the vapor, nanopillar structures having a capillary radius of 270 nm were fabricated after the separator. In the nanopillars, vapor pressure is lower than that at a flat liquid surface. An aqueous solution of 9.0 wt % ethanol was used as a model sample, and concentration of the condensed liquid in the nanopillar was estimated as 19 wt %.

Microfluidic chemical systems have been proved to be effective for rapid and efficient chemical processes.[1] We have investigated continuous flow chemical processings (CFCP) on microfluidic chips utilizing micro unit operations (MUOs).[2] Most of conventional MUOs are operations for liquid-phase processes, and a few gas/liquid-phase operations have been developed.[3]

In order to extend applicability of microfluidic chemical systems, development of MUOs for gas/liquid systems, such as evaporation and condensation, have been important. Generally, we should consider pressure and mass balances in the flow control. The gas–liquid flow systems have difficulties in operating in a micrometer-sized restricted space because of large volume change due to phase transition and incompressibility of the gas phase. In addition, it is difficult to trigger the transition and to regulate the position of it. For establishing microfluidic design, position-regulated operation is preferable, but it requires some innovation.

In this letter, we have developed evaporation and condensation. For development of position-regulated condensation, we propose an operation based on capillary condensation in nanofabricated structure. In order to realize the operation, a combination of micro- and nanofabrication is applied.

Figure 1a shows an illustration of a microchip designed for evaporation and condensation. In this design, liquid flow is fed from the interface port #1 to #5 defined in the figure. Figure 1b shows an expanded view of the evaporation zone between points a and b in Figure 1a. When the liquid reaches the evaporation microchannel, the liquid begins to evaporate to generated saturated vapor with a saturated pressure on flat surface, p_0. After separated from the liquid phase, the saturated vapor is transferred from point b to point c. Figure 1c shows the condensation zone between points c and d in Figure 1a. In the condensation zone, the saturated vapor contacts the nanopillars fabricated between the microchannels. When a contact angle of the corresponding liquid, θ, is less than 90°, the saturated vapor pressure in the

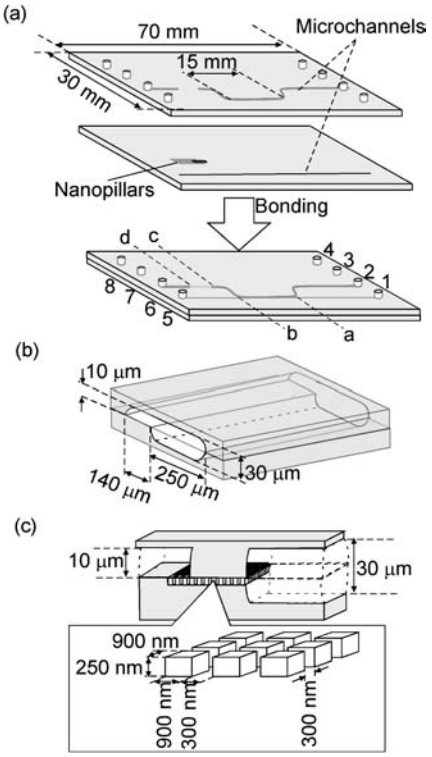

Figure 1. (a) Illustration of the fused-silica microchip. (b) Expanded view of the evaporation zone. (c) Expanded view of the condensation zone.

nanostructure, p_r is less than p_0 as,

$$\ln \frac{p_r}{p_0} = -\frac{2V_m \gamma \cos\theta}{RTr} \quad (1)$$

where V_m, γ, and r are molar volume, surface tension, and capillary radius of the nanopillars, respectively.[4] Therefore, the saturated vapor in the microchannel becomes supersaturated vapor in the nanopillars. Thus, condensation is expected to be triggered in the nanostructure.

In order to realize the design in Figure 1, we have optimized fabrication procedures. In this study, fused-silica substrates having a dimension of 30 mm × 70 mm and a thickness of 0.7 mm were used. The microchannels were fabricated by a photolithographic wet etching method,[2] and then the nanopillars were fabricated by electron-beam-lithography and plasma etching.[5]

In a previous report,[3] we found that shallow microchannels

are effective for gas/liquid separation. In the case of fused-silica substrates, we have not succeeded in two-step wet etching, which was applied to borosilicate glass.[3] In this study, the top and bottom plates were etched with different widths. After thermal bonding, deep (250-μm-wide and 30-μm-deep) and shallow (140-μm-wide and 10-μm-deep) gas/liquid separation microchannel were obtained as shown in Figure 1b.

In order to prevent intrusion of liquid phase, surface of the shallow part was modified with fluoride resin (FS-1010, FluoroTechnology). By using this modification, contact angle over 90° was obtained for temperature range up to 100 °C.

In the condensation area, nanopillars were fabricated on the bottom plate after the microfabrication and the microchannels having appropriate gap were fabricated on the top plate. After thermal bonding, the microchannels were connected through the nanopillar structure as shown in Figure 1c. The single nanopillar has a dimension of 900 nm × 900 nm and a height of 250 nm, and the vacant channel part has a width of 300 nm and depth of 250 nm. From the dimensions, capillary radius, r, was calculated as 270 nm.

For demonstration of the present microfluidic system, evaporation and condensation of water was observed. The microchip was set on a temperature control stage working at 100 °C. The ratio of the saturated pressure of water at 100 °C, p_r/p_0, was calculated as 0.995. After 1 min from the water introduction, we observed the condensation in the nanopillar region as expected, while condensation was not observed in the microchannel area. We have succeeded to demonstrate evaporation and condensation with pure water.

Then, 9.0 wt % aqueous ethanol solution was introduced to the microchip. The temperature stage was working at 78 °C in order to discuss effect of capillary condensation in the nanopillars. The solution was driven with a volume flow rate of 2.0 μL/min for 120 min. Figure 2a shows a micrograph of the condensation zone before operation. Since tilted illumination was applied, purple diffraction light was observed from the vacant nanopillars. Figure 2b shows a micrograph during the condensation. A part of the purple area turned to gray. The contrast change corresponds to reduction of refractive index contrast, which means that the vacant nanopillars were filled with condensed liquid in the gray area. Figure 2c shows the micrograph after the operation. The nanopillars were filled with condensed liquid, and a small portion of liquid was observed in the microchannel.

In order to discuss the operation, the solution passing through the evaporation microchannel drained from the interface #5 in Figure 1a was analyzed because the volume of the condensed solution was too small to handle. The concentration and volume of the solution were 8.6 wt % and 231 μL, respectively. From the input and output volumes, the distillation ratio was estimated as 3.7%. The concentration of the condensed solution calculated by considering mass balance of ethanol and estimated as 19 wt %. Although more efficient distillation is expected after optimization, we have demonstrated microchip distillation by combining original gas/liquid separation and capillary condensation methods.

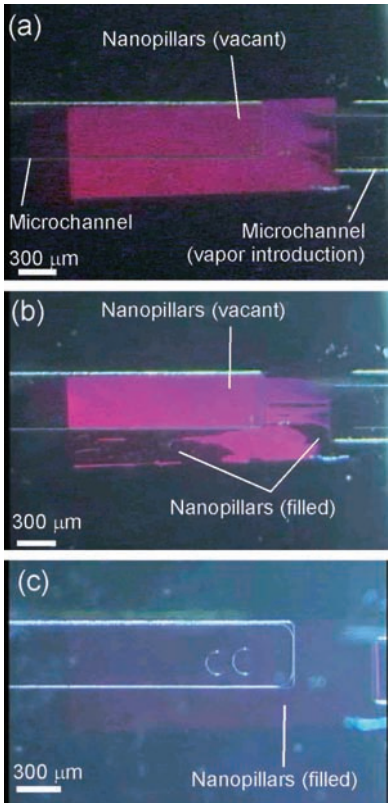

Figure 2. Micrographs of the nanopillars before (a), during (b), and after (c) the operation.

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